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Quadrupole Coupling Constants in the Symmetric Tetrasubstituted Germanes

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Synopsis. The quadrupole coupling constants in the symmetric tetrasubstituted germanes, GeR_4 (R=CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, Cl, and Br) were obtained by measuring the ^{73}Ge spin-lattice relaxation times (T_1) and the reorientational correlation times (τ_c) of the chloroform solutions. Quadrupole coupling constants of GeR_4 were in the range of 0.72 MHz (R=n-C_4H_9) to 1.51 MHz (R=CH_3), and these decreased slightly as the molecular radius increased.

Very little had been reported on the relaxation mechanism of ^{73}Ge nuclei (I=9/2)[1,2] when we[3] started to study this subject. Since then we analyzed the relaxation mechanism of ^{73}Ge in such symmetrical tetrasubstituted germanes as GeR_4 (R=H, CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, Cl, Br, and I).[4–6] We demonstrated that the spin-lattice relaxation of ^{73}Ge in all compounds investigated and the spin–spin relaxation of ^{73}Ge in compounds except GeH_4, $GeCl_4$, $GeBr_4$, and GeI_4 occur solely via the quadrupole relaxation mechanism. The spin–spin relaxation of ^{73}Ge in GeH_4, $GeCl_4$, $GeBr_4$, and GeI_4 were found to occur via a combination of quadrupole and scalar coupling relaxation mechanisms.

During this investigation we noticed that very few quadrupole coupling constants have so far been reported for organogermanium compounds.[1] The quadrupole coupling constants in the crystal or powder states are generally obtained from Mössbauer or NQR (nuclear quadrupole resonance) spectra. If electric field gradients occur at the central germanium nuclei, and if correlation times are obtainable in the symmetric tetrasubstituted germanes mentioned above, the quadrupole coupling constants of ^{73}Ge in the liquid state can be estimated from the relaxation times and the correlation times. In this paper we describe our attempts along this line.

Experimental

Preparation of Compounds. Tetraalkylgermanes were prepared by the procedures described in the literature.[7] $GeCl_4$, guaranteed reagent grade, was purchased from Sumitomo Metal and Mines Co., Ltd. $GeBr_4$ (bp 82—83 °C/32 mmHg; 1 mmHg≈133.322 Pa) was synthesized by the procedures described in the literature.[8] The purity of the compounds were confirmed by ^1H NMR spectra (Varian EM-390) and/or GLC (Shimadzu GC-3BT). GeR_4 were dissolved in $CDCl_3$ (50% v/v). The solution was taken in an egg shaped cell and degassed by the freeze-thaw method.

Germanium-73 NMR Spectra. The ^{73}Ge NMR spectra were recorded by JEOL FX-90Q equipped with a low frequency insert NM-IT10LF at 3.10 MHz. T_1 was determined by the inversion-recovery method. The error in T_1 thus determined was estimated to be about or less than 5%. Other conditions of the measurements have been described in previous papers.[5,6]

Measurement of Viscosity. For the measurement of viscosity of GeR_4, the sample was dissolved in $CHCl_3$ (50% v/v). The procedure of the measurement has been described in the previous papers.[5,6]

Estimation of Molecular Radius. The radius of GeR_4 (R=alkyl) is defined as the distance between the germanium nucleus and the terminal hydrogen atom plus van der Waals radius of terminal hydrogen atom. The germanium–hydrogen distance was obtained from the structure of the alkylgermanes optimized by the molecular mechanics calculations[9] while for GeR_4 (R=halogen) the reported values for germanium–halogen distance were used.[10,11]

Results and Discussion

Origin of Relaxation. It is generally accepted that if electric field gradients occur at the nucleus site, the quadrupole relaxation times, T_1 and T_2, of nuclei with nuclear spin I>1/2 are related to the reorientational correlation time τ_c at the extreme-narrowing limit as given below:[12]

$$\pi\Delta\nu_{1/2} = \frac{1}{T_1} = \frac{1}{T_2} = \frac{3\pi^2}{10}\,\frac{2I+3}{I^2(2I-1)} \times \left(\frac{e^2Qq}{h}\right)^2\left(1+\frac{\zeta^2}{3}\right)\tau_c \qquad (1)$$

where e^2Qq/h is quadrupole coupling constant and ζ is asymmetry parameter.

Since tetrasubstituted germanes of the type GeR_4 have tetrahedral symmetry, the electric field gradient at the germanium nuclei must be zero, which is expected to make the relaxation time of germanium nuclei infinitely long. The fact is, however, that the relaxation time is finite.

Some authors have proposed a theory to account for the quadrupole relaxation of symmetric molecules. Brown and Colpa suggested that the quadrupole relaxation occurs by the vibration and/or rotation,[13] while Osten and Jameson attributed the effect to the collision among molecules.[14] The electric field gradient generated at the germanium nuclei of symmetric tetrasubstituted germanes is averaged to zero but it has a non vanishing mean square, i.e., $(e^2Qq/h)^2 \neq 0$.[14] Osten and Jameson calculated the relaxation rate of neat $GeCl_4$ at 300 K by using the collision model as $1/T_1 = 2\ s^{-1}$ comparable with the observed rate ($1.2\ s^{-1}$).[2] Sekatsis et al. suggested that the non-zero electric field gradient is induced by the deformation of the molecular orbitals during molecular collisions.[1] Tarasov et al.[2] suggested that the quadrupole relaxation of $GeCl_4$ and $GeBr_4$ was affected by the vibrationally-induced electric field gradients. We have also shown in previous papers[3–6] that T_1 of ^{73}Ge compounds investigated are predominantly governed by the quadrupole relaxation mechanism. If the reorientational correlation time can, for instance, be determined from the viscosity

Table 1. The Values of the Concentration, Density, Viscosity, and Radius of Tetrasubstituted Germanes

Compd	Concn	ρ (30 °C)	η (30 °C)	r
	mol dm^{-3}		cP$^{a)}$	Å
GeMe$_4$	3.67	1.26	0.537	3.75
GeEt$_4$	2.63	1.21	0.573	5.11
GePr$_4$	1.95	1.20	0.720	5.83
GeBu$_4$	1.55	1.19	0.910	6.90
GeCl$_4$	4.37	1.67	0.586	3.89
GeBr$_4$	4.02	2.29	0.986	4.24

a) 1 P=0.1 Pa s.

data, it is tempting to employ Eq. 1 as a means to estimate the quadrupole coupling constants of organogermanium compounds in solution. Some authors have interpreted the quadrupole relaxation data associated with highly symmetric nuclei, such as ^{55}Mn(CNR)$_6^{+\text{ or }2+}$, (R=i-C$_3$H$_7$ and t-C$_4$H$_9$),[15] aqueous tetrahedral oxoacid anions MO$_4^{X-}$ (M=^{51}V, ^{53}Cr, ^{97}Mo, ^{183}W, ^{55}Mn, ^{99}Tc, ^{185}Re, ^{189}Os, X=1, 2, 3),[16,17] and chloride ion[18—20] and halide ions[21] by Eq. 1.

At the moment, we believe that Eq. 1 may be extended to the assessment of the quadrupole coupling constants of highly symmeteric molecules as has previously been done by several investigators[15—21] mentioned above.

Quadrupole Coupling Constants. We estimated the quadrupole coupling constants of GeR$_4$ with the aid of Eq. 1. The values of the concentration, density (ρ), viscosity (η), and radius (r) of tetrasubstituted germanes are shown in Table 1. The correlation time, τ_c is given by Eq. 2,[22]

$$\tau_c = 4\pi r^3 \eta f/3kT \tag{2}$$

where k is the Boltzmann constant, T the absolute temperature, and f a microviscosity which is described in the previous papers.[5,6,22] The mean radius of solvent molecule CHCl$_3$ was estimated as 3.13 Å.

The quadrupole coupling constants for GeR$_4$ were found in the range of 0.72 to 1.7 MHz as shown in Table 2. For Ge(CH$_3$)$_4$ and Ge(C$_4$H$_9$)$_4$ in CDCl$_3$, the values of quadrupole coupling constants have been reported as 1.7 and 1.1 MHz, respectively,[1] in which τ_c was calculated from dipole–dipole interaction of CH$_3$ group. This discrepancy of the quadrupole coupling constants may be due to the different methods of determining τ_c values.

Since the relaxation rate is proportional to the correlation time and to the square of the quadrupole coupling constant, it is interesting to determine which of the two mainly determines the relaxation rate.

We found that the difference of relaxation rate is mainly governed by the correlation time rather than by the quadrupole coupling constant from the data for GeR$_4$ shown in Table 2.

A linear relationship exists between ln τ_c and the molecular radius as shown in the previous paper.[6] On the other hand, the value of quadrupole coupling constant slightly decreases as the molecular radius increases. In Fig. 1 a plot of the quadrupole coupling constants vs. molecular radius, r is given. The larger is the radius, the smaller is the quadrupole coupling constant. It seems that in symmetrical germanium compounds investigated the smaller complex molecule will be instantaniously distorted by the molecular vibrations and rotations, or collisions. On the other hand, for octahedral manganese isocyanide complexes, the differences in the line widths were attributed to variable values of quadrupole coupling constants under the assumption that the correlation time is essentially independent on the shape and size of similar molecules.[15] Indeed, Nielson et al. showed that wider half widths were observed for the complexes with larger ligands whereas molecules with large complex ligands tend to distort due to vibrational and rotational movements.[15]

Table 2. The Values of T_1(IR), and τ_c, and e^2Qq/h of Tetrasubstituted Germanes

Compd	T_1(IR)	τ_c(30 °C)	e^2Qq/h
	ms	10^{-11} s	MHz
GeMe$_4$	290	0.69	1.51
GeEt$_4$	220	2.2	0.97
GePr$_4$	100	4.5	1.00
GeBu$_4$	80	10.9	0.72
GeCl$_4$	280	0.78	1.45
GeBr$_4$	160	1.8	1.25

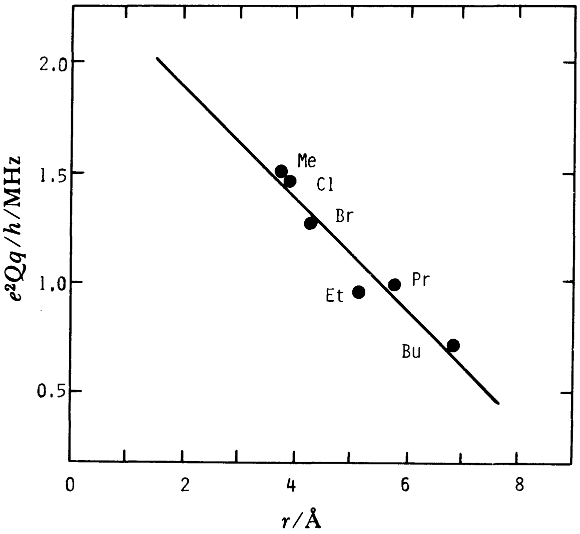

Fig. 1. Plot of e^2Qq/h. vs. radius of GeR$_4$.

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